

DEGRADATION OF DISLODGEABLE FOLIAR
RESIDUES OF METHAMIDOPHOS ON CAULIFLOWER
AND BROCCOLI IN VENTURA
AND SAN LUIS OBISPO COUNTIES IN 1984

By

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SUMMARY

During October of 1984, one cauliflower and three broccoli fields were treated with Monitor 4, then monitored for foliar decay of methamidophos. Dislodgeable residue from the leaf surface was monitored for at least one week. Sample results indicated that under the conditions of this study the reentry interval of 24 hours may be adequate to safeguard unprotected fieldworkers based on the current estimated safe level for methamidophos. Nondetectable levels were seen as early as seven days after the application in one field while another field still had detectable levels after 14 days.

INTRODUCTION

In June 1971, the California Department of Food and Agriculture established reentry intervals for specific crop/pesticide combinations. A reentry interval is the time period that must elapse between the application of a pesticide and the entry of unprotected workers into the treated area. This waiting period was instituted to allow sufficient time for toxic materials to environmentally degrade to a lower hazard residue level. This study was conducted to monitor the foliar decay rate of methamidophos and evaluate the current safety interval of 24 hours.

Methamidophos is a broad spectrum systemic insecticide, used widely for agricultural pests. It is sold in California in two products (Ortho Monitor 4 Spray, EPA Registration #239-2404-AA, and Monitor 4, EPA Registration #3125-280-AA). Both products are emulsifiable concentrate Category I pesticides containing four pounds of active ingredients per gallon and display the signal word "Danger" on the label. The oral LD₅₀ (rat) of technical grade methamidophos is 7.5 mg/kg (NIOSH) and the dermal LD₅₀ (rat) is 50 mg/kg (Frear).

METHODS

With assistance from the Ventura and San Luis Obispo County Agricultural Commissioners' staff, and local Pest Control Operators (PCO), four fields treated with Monitor 4 were monitored. Three broccoli fields and one cauliflower field were each monitored for foliar decay of methamidophos for a two week period after the application or until nondetectable levels were reached. Three of these fields received the maximum label rate of 2 pints (1.0 lbs. a.i.) of Monitor 4 per acre and the other field received 1 pint (0.5 lbs. a.i.) of Monitor 4 per acre. All applications were applied by ground in a tank mix of 60 to 100 gallons of water per acre. Each field was divided into three areas. A fifty foot section of one row from each area was selected and identified with markers for sampling. Three replicate samples were taken each time the field was sampled. Each replicate sample consisted of 45 leaf punches, a composite of 15 leaf punches from each of the three marked rows. The samples were collected using a 2.5 cm disk leaf punch which was cleaned with alcohol between samples. A pre-application sample was taken the day before, or the morning of, the application. The first post-application sample was taken 1 to 4 hours after the application then again daily for up to 4 more days. One more sample was collected approximately seven days after the application then again at 14 days if the seven day sample was above the detection limit. All samples were collected in jars and sealed with aluminum foil, then placed on ice for shipment to Chemistry Laboratory Services in Sacramento for next-day analysis. Application parameters, irrigation schedules, and crop for each plot are reported in Appendix A.

The daily high and low air temperatures and precipitation were recorded by nearby local weather stations and made available through the National Weather Service (Appendices B and C.)

Laboratory analysis consisted of stripping the leaf disc surfaces using a water and surfactant solution. The resulting aqueous solution was brought to a known final volume and a 20% aliquot was taken and blended with ethyl

acetate and sodium sulfate. The ethyl acetate was then evaporated to a desired volume and analyzed by gas chromatography.

RESULTS AND DISCUSSION

The analytical results for each composite sample and the averages for each day are presented in Table 1. The minimum detectable level (0.001 ug/cm^2) was used in calculating the average of replicates for each sample under the detection limit. Figure 1 shows the average concentrations of the three replicate samples for each field plotted against time as well as the level where an unprotected worker may enter the field.

The current estimated safe level for reentry into a field treated with Monitor is 0.66 ug/cm^2 of leaf surface (Maddy, 1985). At this level, an unprotected worker may enter a field to conduct work involving substantial foliage contact and should not experience any acute or chronic illness symptoms. This number was extrapolated using the parathion dermal LD_{50} and the parathion safe level as a reference point.

Current regulations state that workers may not enter a field treated with methamidophos for 24 hours after the application. This is based on the potential for methamidophos to cause acute cholinesterase inhibition and relatively low frequency of illnesses associated with it.

The data presented here suggest the current reentry interval may be adequate based on the estimated safe reentry level of 0.66 ug/cm^2 for methamidophos. No sample in the entire data set was above this estimated safe level. The data from plots 1 and 3 fluctuated somewhat. The levels found at days 1 and 2 after the application were two to three times higher than the initial samples taken immediately after the application. This suggests that there was high variability in the concentrations in these fields and the sample size collected may have been too small to adequately estimate the average concentration. Plots 2 and 4 however, show a more normal decay rate.

TABLE 1

Results of samples collected for each field reported in micrograms of
Monitor per square centimeter of leaf surface.

			Days after Application							
		Presample	1 to 4 Hours	1	2	3	4	5	6	7 14
Plot 1	rep 1	ND	.095	.450	.196	.140	.051			.015 .017
	rep 2		.091	NS	.237	.124	.078			.007 .008
	rep 3		.177							.012 .013
	mean		.121	.340	.237	.113	.066			.011 .013
Plot 2	rep 1	.013	.171	.113	.118	.057				.020 ND
	rep 2		.129	.116	.102	.035				.017 ND
	rep 3		.230	.123	.115	.019				.028 ND
	mean		.171	.117	.112	.037				.022 .001
Plot 3	rep 1	ND	.048	.051	.125			.013	.007	ND
	rep 2		.069	.043	.109			.010	.005	ND
	rep 3		.047	.097	.155			.009	.008	ND
	mean		.055	.064	.130			.011	.007	.001
Plot 4	rep 1	ND	.200	.134	.112	.054				ND
	rep 2		.202	.137	.071	.045				ND
	rep 3		.390	.138	.087	.040				ND
	mean		.284	.136	.090	.040				
mean for all fields			.159	.148	.142	.065	.066	.011	.007	.011 .005

NS - Not Sampled

ND - None Detected (The detection limit was 0.001 ug/cm²; this value was used
in calculating means with samples below the detection limit.)

1.000

FIGURE 1.

Estimated Safe Level

0.100

Micrograms of Methamidophos per
Square Centimeter of Leaf Surface

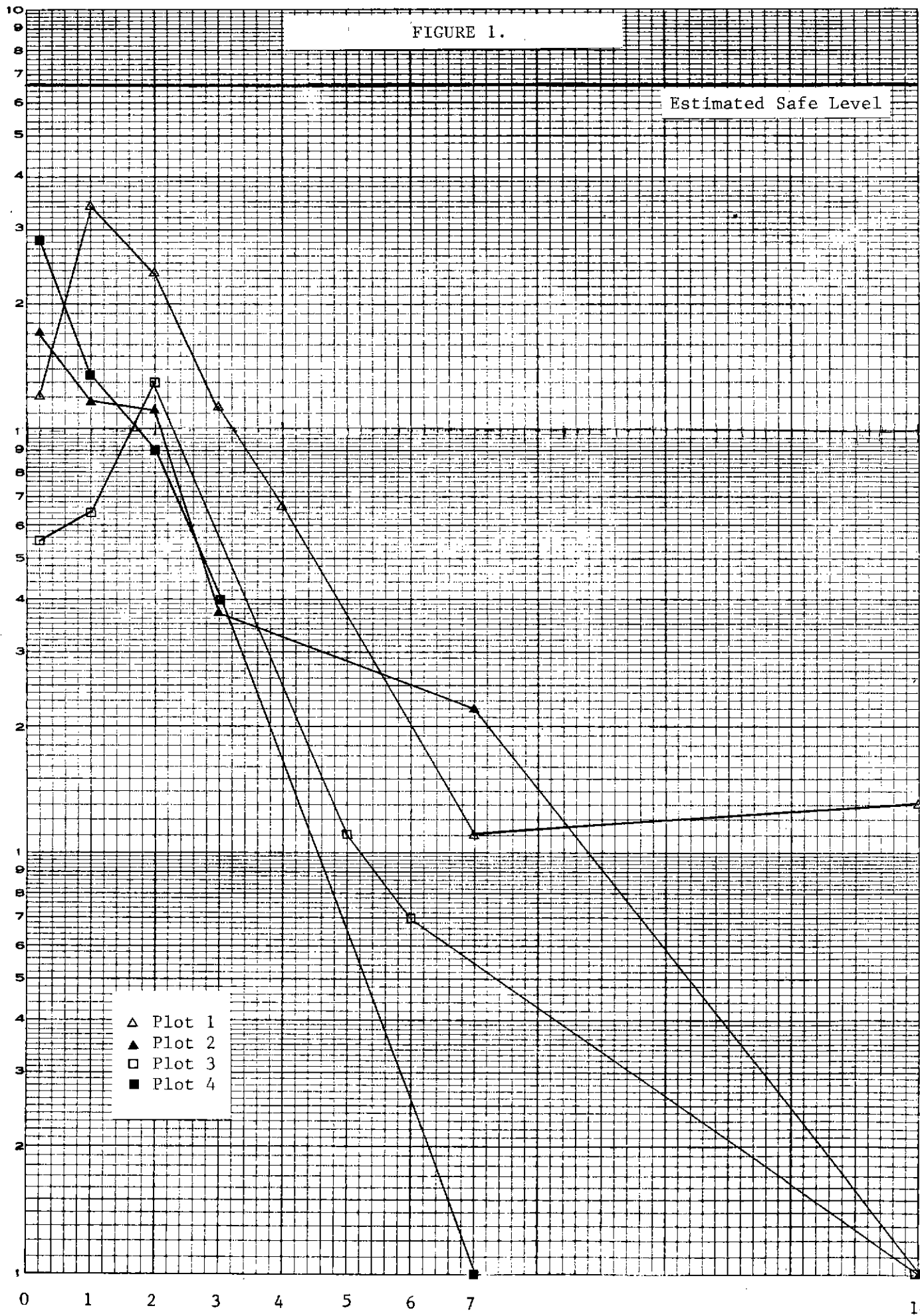
0.010

0.001

- △ Plot 1
- ▲ Plot 2
- Plot 3
- Plot 4

Days After Application

14



APPENDIX A

Application Parameters of Fields Treated With Monitor

<u>Parameter</u>	<u>Plot 1</u>	<u>Plot 2</u>	<u>Plot 3</u>	<u>Plot 4</u>
Application Rate lbs. a.c./Acre	1.0	1.0	0.5	1.0
Dilution	60	100	100	60
Date of Application	10/1	10/2	10/3	10/16
Average Plant Height at Application	3"	12"	12"	6"
Irrigation Method	Furrow	Furrow	Furrow	Furrow
Irrigation During Study Period	10/6	Before 14 Day Sample	10/8	10/20
Precipitation	10/16	10/16	10/16	10/16
Field Location	Ventura	Ventura	Ventura	SLO
Crop	Broccoli	Broccoli	Broccoli	Cauliflower

APPENDIX B

Daily High and Low Air Temperatures and Precipitation
Reported by the Oxnard Weather Station*

<u>Date</u>	<u>High °F</u>	<u>Low °F</u>	<u>Precipitation (Inches)</u>
1	72	56	0
2	74	57	0
3	71	52	0
4	72	55	0
5	74	57	0
6	73	56	0
7	74	56	0
8	70	56	0
9	73	57	0
10	71	62	0
11	72	54	0
12	75	57	0
13	79	57	0
14	78	53	0
15	74	54	0
16	74	55	.34
17	67	48	0
18	70	50	0

*This weather data applies to Plots 1, 2 and 3.

APPENDIX C

Daily High and Low Air Temperatures and Precipitation
Reported by the Santa Maria Weather Station*

<u>Date</u>	<u>High</u> <u>°F</u>	<u>Low</u> <u>°F</u>	<u>Precipitation</u> <u>Inches</u>
16	72	42	.27
17	64	43	0
18	71	47	0
19	70	52	T**
20	68	50	0
21	69	40	0
22	77	40	0
23	80	41	0

*This weather data applied to Plot 4.

**Trace amount

REFERENCES

1. NIOSH. 1983. 1983 Registry of Toxic Effects of Chemical Substances. Vol. 3, p. 127.
2. Frear, E. H., ed., College Science Publications, Pesticide Index, State College, PA, 1969.
3. Maddy, K. T., Estimated Safe Levels of Foliar Pesticide Residues to Allow Unprotected Workers Reentry into Fields in California. California Department of Food and Agriculture. Worker Health and Safety Unit. HS-1280. 1984.